

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 43/40, 33/12, 25/12	A1	(11) International Publication Number: WO 95/02963 (43) International Publication Date: 2 February 1995 (02.02.95)
<p>(21) International Application Number: PCT/EP94/02253</p> <p>(22) International Filing Date: 9 July 1994 (09.07.94)</p> <p>(30) Priority Data: 08/095,122 20 July 1993 (20.07.93) US</p> <p>(71) Applicant (for all designated States except US): BASF CORPORATION [US/US]; 8 Campus Drive, Parsippany, NJ 07054 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): JÄGER, Karl-Friedrich [DE/DE]; Chenover Strasse 7, D-67117 Limburgerhof (DE). KILBRIDE, Terence, Jr. [US/US]; 5501 Lakeview Drive, Bloomfield Hills, MI 48302 (US). LISA, Rudolph, Ernest [US/US]; 26459 East River, Grosse Ile, MI 48138 (US).</p> <p>(74) Agent: LANGFINGER, Klaus-Dieter; BASF Aktiengesellschaft, D-67056 Ludwigshafen (DE).</p>		<p>(81) Designated States: AU, BR, BY, CA, CN, CZ, FI, HU, JP, KG, KR, KZ, NO, NZ, PL, RU, SK, TJ, UA, US, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i> <i>With amended claims.</i></p>
<p>(54) Title: HIGH CONCENTRATED, SOLID MEPIQUAT CHLORIDE AND CHLORMEQUAT CHLORIDE PRODUCTS</p>		
<p>(57) Abstract</p>		
<p>The present invention provides hygroscopic plant growth regulator formulations in solid forms and associated methods of making the powders and tablets. The most preferred formulation uses an effective amount of an N,N-dimethyl-piperidinium and/or N,N-dimethylammonium salt.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

High Concentrated, Solid Mepiquat Chloride and Chlormequat Chloride Products

5 Description

The present invention relates to methods for making flowable, highly concentrated powders and tablets of hygroscopic plant growth regulator compounds, and more specifically to processes to
10 dry mepiquat chloride and chlormequat chloride aqueous solutions to form flowable highly concentrated solid products.

Plant growth regulators affect the physiology of plant growth and influence the natural rhythm of a plant. More specifically, plant
15 growth regulators may, for example, reduce plant height, stimulate seed germination, induce flowering, promote or inhibit fog, darken leaf coloring, minimize lodging of cereals, slow grass growth on lawns, reduce boll rot and provide better boll retention in cotton.

20 Plant growth regulators may be applied to plants in a variety of methods including different formulations. Of these various methods, use of liquid and dry compositions are the most common. The particular formulation desired and resulting efficacy enhancement will greatly depend upon the species to be treated, environmental conditions, the geographical area and the climatology of the area at the time of treatment.

The plant growth regulator, known trivially as mepiquat chloride,
30 is generally used to control various aspects of cotton boll growth. See, for example, Khafaga, Angew. Botanik 57, 257-265 (1983); Sawan et al., J. Agronomy & Plant Science, 154, 120-128 (1985); U.S. Patents 3,905,798 and 4,447,255; and "The Pesticide Manual", 9th Edition, The British Crop Protection Council, 35 Farnham, Surrey, Great Britain, Entry No. 7920.

The plant growth regulator, known trivially as chlormequat chloride, is generally used to reduce lodging of cereals (cf. "The Pesticide Manual", 9th Edition, The British Crop Protection Council,
40 cil, Farnham, Surrey, Great Britain, Entry No. 2420).

Mepiquat chloride and chlormequat chloride are used as plant growth regulators in agriculture. Mepiquat chloride and chlormequat chloride have high water solubilities of more than 1 kg/L at
45 20°C. The melting point of mepiquat chloride is 223°C, chlormequate chloride begins to decompose at 210°C.

2

Both substances are very hygroscopic, readily absorbing moisture from humid air, so much so, that the dry powders can turn to liquid when exposed to ambient humid air. During storage, the solid mepiquat chloride or chlormequat chloride is strongly caking and sticking to container surfaces, even at low residual water contents of less than 0.5 wt.-%.

These properties make it extremely difficult to dry mepiquat chloride or chlormequat chloride. In conventional spray dryers, the material is very difficult to dry. It must be atomized extremely finely to reduce the moisture to a suitable level and even then it retains too much water to dry practically. The product remains sticky and adheres to the walls of the dryer and the dryer ducts and cyclones, eventually plugging the ducts and cyclones. Furthermore, powder from such a process, because it is so fine, flows poorly out of the dryer, and upon storage in a drum, is rendered unflowable due to caking.

Solid forms of plant growth regulators offer a number of key advantages, including convenience, increased stability and shelf life, as well as reduced packaging, storage and shipping costs.

Additionally, there is the possibility of future government regulation requiring solid forms of agricultural products in order to reduce handling of contaminated packaging of these products during field application and during disposal. These dry flowable plant growth regulating compounds would be safer for the farmer to use and dispose of, and also result in a smaller volume of hazardous waste being produced.

There is a need for dry, flowable, highly concentrated powder and tablet formulations of hygroscopic plant growth regulators.

Surprisingly, free-flowing, non-caking solid mepiquat chloride and chlormequat chloride formulations can be achieved by mixing the solid hygroscopic plant growth regulator with finely divided, highly absorptive inerts. In such mixtures, concentrations of the plant growth regulator of up to about 99 wt.-% are achievable.

When the mixtures of the invention are directly applied in a spray tank, the plant growth regulator dissolves instantly in the water without residues.

The preferred plant growth regulators of the present invention include the group consisting of 1,1-dimethyl-3,4-dehydro-piperidinium bromide, 4-chloro-1,1-dimethyl piperidinium bromide, 1,1-dimethylhexahydropyridazinium bromide, and 1,1-dimethyl-piperidinium chloride, also known as mepiquat chloride and

3

2-chloroethyltrimethylammonium chloride, also known as chlormquat chloride.

It is an object of the present invention to provide an agriculturally acceptable hygroscopic plant growth regulator formulation in a solid form.

It is a further object of the present invention to provide methods of making the solid form of hygroscopic plant growth regulator compositions of the present invention.

It is another object of the present invention to provide an agriculturally acceptable hygroscopic plant growth regulator formulation in the form of a tablet.

15

It is a further object of the present invention to provide methods of making the dry, flowable tablet form of hygroscopic plant growth regulator compositions of the present invention.

These and other objects of the present invention will be more fully understood from the following description of the invention.

Figure 1 illustrates a spray dryer used in a method of the present invention.

25

Figure 2 illustrates a double drum dryer used in a method of the present invention.

Figure 3 illustrates a batch vacuum dryer used in a method of the present invention.

As used herein, the term "agriculturally acceptable" includes agricultural, industrial and residential use.

As used herein, "plant growth regulator(s)" (hereinafter abbreviated as "PGR") or "regulation" includes the following plant responses: inhibition of cell elongation, for example reduction in stem height and internodal distance, strengthening of the stem wall, thus increasing the resistance to lodging; compact growth in ornamentals for the economic production of improved quality plants; promotion of better fruiting; increasing the number of ovaries with a view to stepping up yield; promotion of senescence of the formation of tissue enabling fruit to absciss; defoliation of nursery and ornamental bushes and trees for mail-order business in the fall; defoliation of trees to interrupt parasitic chains of infection; hastening of ripening, with a view to pro-

4

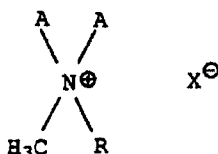
gramming the harvest by reducing the harvest to one to two pickings and interrupting the food-chain for injurious insects.

As used herein, PGR formulations of the present invention may be used to form both package and tank mix compositions.

The present preferred invention comprises PGR compositions comprising an agriculturally and plant growth regulating effective amount of a hygroscopic PGR, and more preferably, an N,N-dimethylpiperidinium or N,N-dimethylammonium salt in a dry flowable highly concentrated powder.

Preferred PGRs include salts of the formula:

15



20

where R is methyl or ethyl; X is the anion of an inorganic or organic, but not phytotoxic acid, preferably bromide or chloride, and the groups A independently denote methyl, ethyl or propyl which independently may be substituted by chloro or bromo, or the groups A together denote a chain of 4 or 5 methylene groups, which chain may be substituted by chloro, bromo, methyl, chloromethyl, bromomethyl, hydroxymethyl, and methylene, or which chain containing one or two double bonds, or A is the chain $-(\text{CH}_2)_n-\text{NH}-$, where n is 3 or 4, disclosed in U.S. Patent 3,905,798 and hereby incorporated by reference.

Preferred specific examples of PGRs include 1,1-dimethyl-3,4-dehydro-piperidinium bromide, 4-chloro-1,1-dimethyl-piperidinium bromide, 1,1-dimethylhexahydropyridazinium bromide, 1,1-dimethylpiperidinium chloride and 2-chloroethyltrimethylammonium chloride.

The most preferred plant growth regulators are 1,1-dimethylpiperidinium chloride, also known as N,N-dimethylpiperidinium chloride or mepiquat chloride, which is commercially available under the registered trademark Pix® (BASF AG, Germany) and 2-chloroethyltrimethylammonium chloride or chlormequat chloride, which is commercially available under the registered trademark Cycocel® (BASF AG, Germany).

45

5

For convenience of description, mepiquat chloride will be used. However, the methods described apply equally to other hygroscopic PGRs, especially to chlormequat chloride.

- 5 In a preferred embodiment, silica is injected in the inlet air stream of a spray dryer at a controlled rate.

A spray dryer of the type illustrated in Figure 1 may be used. As can be shown from Figure 1, the aqueous PGR feed solution is agitated in a feed tank (2) and fed through a line (4) via a feed pump (6) into the spray dryer unit (8). The aqueous PGR feed solution is introduced into the spray dryer unit by an atomizing means (10). An inlet air heating means (12) provides heat to the dryer at a temperature of about 150 to about 250°C.

15

A flow aid such as silica is stored in a feed hopper (14) and injected into the spray dryer unit (8) via a screw feeder (16) through a line by an air eductor (18).

- 20 The silica adheres to the forming droplets or partially dried particles formed by the aqueous mepiquat chloride feed solution in the vicinity of the atomizer (10) and reduces or eliminates the tendency of the partially dried mepiquat chloride particles to stick to the spray drying unit walls (20, 22), the ducts (24), and the cyclone (26). The silica also renders the powder more flowable, eliminating caking in the drum even when stored for long periods of time provided the drum excludes ambient moist air. The flowing powder is then suitable for commercial tabletting or for filling water soluble bags, e.g. made of polyvinyl alcohol (PVA) films and marketed under trademarks as Monosol M7030® or Monosol M8532®.

- 35 The rate at which the aqueous PGR feed solution is fed into the spray dryer unit is not critical and is dependent upon the size of the spray dryer used. This rate is easily determined by those skilled in the art.

- A preferred method dries the mepiquat chloride solution with a double drum dryer as illustrated in Figure 2. The double drum dryer has a pair of hollow, rotating drums (28, 30) whose surfaces are scraped by a knife (32). High pressure steam is introduced to the interior of the drums and mepiquat chloride solution added continuously via a feed line (34) to the nip between the drums (36). The drums turn toward one another, by means of a conveyor, for example 38 depositing a portion of the liquid, boiling mepiquat chloride solution on the drum surface (28, 30) where boiling is initiated. Upon further rotation, the thin film

6

of mepiquat chloride's water boils off into the vapor hood (40) and a solid film remains that is scraped by sharp knife (32) from the turning drum surface (28,30). The material is then collected and the flow aid is added to it to improve flowability and impart
5 anti-caking properties prior to tabletting or filling water soluble bags.

The plant growth regulator feed solution is preferably charged into the double drum dryer at a rate of about 5 gm/min. to about
10 200 gm/min. per square foot (about 9.3 dm²) of heated surface and the aqueous plant growth regulator is preferably charged into the double drum dryer into the nip between the drums.

A preferred embodiment of the drying process utilizes a batch vacuum dryer with chopping blades which can also be described as a
15 mechanical fluid bed. The most preferred batch vacuum dryer is a Littleford® type (or Lödige) vacuum dryer, as illustrated in Figure 3.

20 As is seen from Figure 3, the vacuum dryer unit (52) consists of double jacket (42, 44). Inside the double jacket is a hollow rotating shaft (46) with attached plough shaped mixing elements (48).

25 Aqueous PGR feed solution is fed via a line (50) into the vacuum dryer unit (52). Steam or hot water (54) is fed via a line (56) into a jacket (42) which surrounds the vacuum dryer unit (52), and optionally through the hollow rotating shaft (46). Agitating means (57) in the interior of the vacuum dryer unit (52) agitates
30 the aqueous PGR feed solution. A vacuum means (58), which may be a pump or vacuum jet unit is introduced into and applied to the vacuum dryer unit (52). The vacuum and applied jacket heat causes the evaporation of the water from the aqueous PGR feed solution. The evaporated water boils up, passes through a bag collector
35 means (60), and is recovered by a condenser (62) and collected in a condensate tank (64).

When a sufficient amount of water has been evaporated, a paste begins to form. Mixing elements (48) are used to divide the paste, breaking it up, and bringing the interior moisture to the
40 surface so as to expose it to the vacuum to increase the drying rate. As the material solidifies, the chopping means breaks the material into small particles to maintain the high drying rate.

45 A free-flowing, non-caking solid mepiquat chloride formulation can be achieved by mixing the solid mepiquat chloride with a finely divided, highly absorptive inert flow aid such as silica.

The addition of silica or other flow aid renders the powder flowable and non-caking, and suitable for tableting or filling water soluble bags. The flow aid is introduced manually or mechanically through a port on or near the top of the drying chamber.

5

All three drying processes use silica or other flow aid to improve flowability and prevent caking. These inert additives include any form of silica including fumed silicas, precipitated silicas, aluminum silicates, magnesium silicates, and the like, zeolites, bentonites, montmorillonites, and attapulgites and mixtures thereof. The most preferred silica is commercially available as Sipernat® 50S, which is a synthetic amorphous silicon dioxide hydrate.

15 The weight of silica per weight of mepiquat chloride in all of these drying processes is about 0.2:100 to 3:100, and more particularly, about 2:100.

Optionally, to further improve flowability, reduce sticking tendency or caking, or to increase the dissolution rate, binders, fillers, and/or disintegrants can be dissolved in the feed solution before drying.

Suitable binders, fillers, and/or disintegrants include water-soluble cellulose derivatives, cellulose derivatives, carboxymethyl cellulose, hydroxypropyl methylcellulose, water soluble gums such as gum arabic, gum tragacanth, alginates, gelatin, and polyvinylpyrrolidone, cross-linked polyvinylpyrrolidone, microcrystalline cellulose, modified starches such as sodium carboxymethyl starch, and mixtures thereof.

Preferred binders, fillers, and/or disintegrants are carboxymethyl cellulose.

35 Other suitable fillers, binders, and/or disintegrants include any water soluble starch, corn syrup, dextrin or pregelatinized starch which is at least partially soluble in water at ambient temperature. For example, there can be used as a binder the pregelatinized, modified and stabilized waxy maize starch which is marketed by the National Starch and Chemical Corporation under the trade name Instant Celar Gel®. In addition, pregelatinized corn starch marketed by the Hubinger Company under the trade name OK Pre-Gel® can be used. Other binders suitable for use are pregelatinized food starch, refined from tapioca and marketed under the trade name Instant Gel®; stable, modified amylopectin marketed under the trade name Kosol®; a low viscosity tapioca dextrin marketed under the trade name Crystal Gum®; dextrinized corn

starch marketed under the trade name Purity Glaze®; maltodextrin marketed under the trade name Maltrin®, such as M040 by Grain Processing corporation.

- 5 The preferred amount of binders, fillers, and/or disintegrants in the feed solution is from about 0.1 to about 99.7 wt.-%.

All of the above-described powders, with and without fillers, binders, and/or disintegrating agents can then be tabletted or
10 filled into water soluble bags. Unexpectedly, the high potency powders which contain only the hygroscopic PGR active material and silica flow aid, tablet without aid of binders, fillers, and/or disintegrants, or lubricants on a commercial tablet press. The tablets formed are of commercial quality, having reproducible
15 weight, sufficient tablet strength, and acceptable solubility.

Water absorbance is minimal provided that the tablets are made in a dehumidified room. The tablets can be dissolved and passed through a 50 mesh screen such as that found on spray equipment
20 without residue.

While the ratios of the concentrations of the various components of the present invention hereinafter suggested, those skilled in the art will recognize that minor variations may be necessary to
25 accommodate particular characteristics of acceptable plant growth regulators which may be employed in this invention.

In general, the formulations of the present invention contain from about 0.1 to about 99.8 wt.-%, and preferably from about 95
30 to about 99 wt.-% of active ingredient.

Typically, for a plant growth regulator concentrate of the present invention, the concentration of regulator active ingredient will be at least 6 ml/acre (about 0.0125 pints/acre).
35

In such mixtures, concentrations of mepiquat chloride up to about 99 wt.-% are achievable. When the mixtures of the invention are directly applied in a spray tank, the mepiquat chloride dissolves instantly in the water and this spray solution passes a 50 mesh
40 screen of the spray equipment without residues.

The tablets can be manufactured by compressing the mixtures on tablet machines. Also for tableting, other inert ingredients like disintegrants, binders, fillers, and/or disintegrants, wet-
45 ting agents or lubricants can be blended with the PGR mixture. (Optionally, the wetting agents and lubricants can be incorporated by addition in the drying step--either into the PGR liquid

solution before drying, or can be added with the inert flow aid during drying.)

When the tablets are dropped into the water of the spray tank,
5 the mepiquat chloride is quickly dissolved and this spray solution passes a 50 mesh screen of the spray equipment without residues.

In addition to the above-described components, the compositions
10 of the present invention may also include other ingredients or adjuvants commonly employed in the art.

Examples of such ingredients include drift control agents, defoaming agents, preservatives, surfactants, fertilizers, phytotoxicants, herbicides, pesticides, insecticides, fungicides, wetting
15 agents, adherents, nematocides, bactericides, trace elements, synergists, antidotes, mixtures thereof and other such adjuvants well known in the plant growth regulator art.

20 However, it is preferred to employ the compositions of the present invention along with sequential treatments with these other components for optimal effect.

The compositions of the present invention may be applied to
25 plants. The application of liquid and particulate solid plant growth regulator compositions to above ground portions of plants may be carried out by conventional methods, for example, boom and hand application, including sprayers or dusters. The composition may be applied aerially as a spray, if desired. The mixtures of
30 the present invention are preferably used in the form of aqueous solutions. The mixtures are applied in a conventional manner, for example, by spraying, atomizing, watering or disinfecting seed.

The forms of application depend entirely on the purpose for which
35 the compositions are being used. In any event, they should ensure a fine distribution of the active ingredients in the composition.

The above plant growth regulator formulation may then be dispersed in water and sprayed onto plants according to the method of
40 the present invention.

Powders, dusts and broadcasting agents may be prepared by mixing or grinding the active ingredients with a solid carrier.

45 Granules, for example, coated, impregnated or homogeneous granules, may be prepared by bonding the active ingredients to solid carriers. Examples of solid carriers are mineral earths such as

10

silicic acid, silica gels, silicates, talc, kaolin, Attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground plastics, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, and ureas, and vegetable products such as grain flours, bark meal, wood meal, and nutshell meal, cellulosic powders, and the like.

The action of the compositions of the present invention are optimal even at low application rates. For a given plant growth regulator composition, the skilled artisan will readily arrive at a composition having the optimum ratio of the ingredients by routine experimentation. The compositions of this invention may be prepared, for example, by adding, in any order, the various components of the composition of the present invention. For example, one may start with a commercial formulation of mepiquat chloride, which is an aqueous concentrate containing 42 gms/l (about 0.35 pounds per gallon (US)) of mepiquat chloride (4.2 wt.-%). Thereafter, in any order, one mixes suitable amounts of any optional adjuvants or ingredients.

The following examples serve to illustrate the invention and should in no way be construed as limiting the scope thereof.

25 Examples

Example 1 - Formulation

An aqueous solution of mepiquat chloride was dried to give a solid mepiquat chloride with a water content of 0.2 wt.-%. This product was not free flowing and caked in a sealed, tight container after 2 days of storage at room temperature. Directly after drying, 198 g solid mepiquat chloride were mixed with 2 g of Aerosil® 200 (highly dispersible, pyrogenic silicic acid, from DEGUSSA, Germany) in a laboratory mixer to give a homogeneous mixture. After storage in a sealed container for 1 month at room temperature and 50°C, there was no caking.

The mixture remained free flowing. Twenty grams of the mixture were poured into a laboratory spray tank filled with about 3.8 liters (1 gallon) tap water at room temperature. The mepiquat chloride dissolved completely within 1 minute. There was no residue on a 100 mesh screen of the laboratory spray tank.

Example 2 - Water Soluble Bag

One hundred grams of the mixture described in Example 1 were packaged using a bag made of a water soluble polyvinyl alcohol film (Monosol® M7030, from Chris-Craft Industries, USA). This water soluble bag was dropped into a spray tank filled with about 95 liters (25 gallons) tap water at room temperature. The water was circulated through a 50 mesh screen. The mepiquat chloride and the film of the bag dissolved completely within 10 minutes. There was no residue on the 50 mesh screen.

Example 3 - Tablet Formulation

Ninety-five grams of the mixture described in Example 1 and 5 g Divergan® F (finely powdered, crosslinked polyvinyl pyrrolidone, from BASF Corporation, USA) were blended in a laboratory mixer. A 15 g tablet, 5.7 cm (2 1/2 in.) diameter, was made with a hand operated hydraulic press. The tablet was dropped into a spray tank with tap water at room temperature. The tablet broke up completely and the mepiquat chloride dissolved within 10 minutes. There was no residue on the 50 mesh screen of the spray tank.

Example 4 - Formulation

Directly after drying as described in Example 1, 294 g solid mepiquat chloride were mixed with 6 g Sipernat® 50 S in a laboratory mixer to give a homogeneous mixture. After storage in a sealed container for 1 month at room temperature and 50°C, there was no caking. The mixture remained free flowing.

Twenty grams of the mixture were poured into a laboratory spray tank filled with about 3.8 liters (1 gal.) tap water at room temperature. The mepiquat chloride dissolved completely within 1 minute. There was no residue on the 100 mesh screen of the laboratory spray tank.

Example 5 - Water Soluble Bag

One hundred grams of the mixture described in Example 4 were packaged using a bag made of a water soluble polyvinyl alcohol film (Monosol® M8532, from Chris-Craft Industries, USA). This water soluble bag was dropped into a spray tank filled with about 95 liters (25 gallons) tap water at room temperature. The water was circulated through a 100 mesh screen. The mepiquat chloride and the film dissolved completely within 10 minutes. There was no residue on the 100 mesh screen.

12

Example 6 - Tablet Formulation

Using the mixture of Examples 4, 20 g tablets, 5.7 cm (2 1/2 in.) diameter, were made with a hand operated hydraulic press. Five tablets were dropped into a spray tank filled with about 95 liters (25 gallons) tap water at room temperature. The tablets broke up completely and the mepiquat chloride dissolved within 12 minutes. There was no residue on the 100 mesh screen of the spray tank.

10

Example 7 - Formulation

A 600 g/l solution of mepiquat chloride was placed in an agitated, jacketed, spray dryer feed tank and heated to 65°C with tempered water. The heated solution was pumped at 125 g/min to an atomizing wheel rotating at about 17,000 rpm in a spray dryer (a Niro Utility for example). Silica (Sipernat® 50S) from a loss-in-weight screwfeeder was injected via an air eductor into the air plenum to mix with the heated air entering the plenum. The silica was fed at a rate of 4 wt.-% based on the dry basis feed rate of the mepiquat chloride solution. The silica/air mixture, at 200°C, then entered the drying chamber, intermixing with the droplets formed by the atomizer. The resultant outlet temperature is about 140°C. On drying the powder exits the drying chamber does not adhere to the walls of the spray dryer, the ducting, or the cyclone separator. The powder remains flowable in a polyethylene bag packed in a sealed plastic drum.

The resulting powder was flowable, had a moisture content of 0.25 wt.-%, a bulk density of 0.29 g/ml untapped, 0.38 g/ml tapped, and an ash content of about 2 wt.-%. The powder assayed at about 97 wt.-% mepiquat chloride.

Example 8

35

Steam at 105 psig was introduced to a lab scale double drum dryer and the rolls rotated at about 5 rpm. Mepiquat chloride liquid was fed from a reservoir to the nip of the rolls at a rate of about 36 g/minute. The material adhered to the rolls and the moisture was evaporated while the drums rotated. The solid film was scraped off the rolls by a blade and collected. Material collected without silica rapidly caked. Material that was collected and mixed with about 2 wt.-% (Sipernat® 50S) silica did not cake and was flowable. The moisture content was about 1.2 wt.-% in the resultant powder, with a density of 0.25 g/ml untapped and 0.35 g/ml tapped.

13

Example 9

To a 130 liter Littleford "mechanical fluid bed" dryer (Model FKM-130 with chopping blade), about 78 kilograms (171.6 lbs) of mepiquat chloride 600 g/l aqueous solution was charged. The agitator plough was started at 155 rpm, and 15 psig steam introduced to the jacket. A vacuum was pulled with a vacuum pump, maintaining 600 mm Hg at the pump. The evaporated vapors passed through a bag filter and were condensed using a cold glycol/water mixture on the shell side of a condenser. The resulting condensate was collected in a receiver.

As evaporation continued, the amperage drawn by the plough motor began to rise. The chopper blades were turned on, and the drying completed. During this time the steam pressure on the jacket was progressively increased to drive off the water from the forming paste. As more water was removed, the paste turned to solid, the chopper greatly increasing the rate of drying by dividing moist material and exposing the interior moisture to the vacuum and hot dryer walls. When water was no longer being removed, the dried solid was cooled by applying cool water to the jacket of the apparatus. Approximately 2 wt.-% of silica was then added to the material and allowed to blend. When this mixing operation was complete, the finished product was discharged to a drum.

The resulting free flowing powder was composed of particles ranging from approximately 5 to 60 microns in diameter, with a moisture of about 0.08 wt.-%, and bulk density of 0.63 untapped and 0.79 tapped, and ash content of about 2 wt.-%. The powder assayed at about 97 wt.-% mepiquat chloride. There was no detectable mepiquat chloride in the overhead condensate.

Example 10

About 4.5 kilograms (10 pounds) of powder made by the method in Example 9 was charged to the feed hopper of a single station ex-center tablet press (Stokes R type for example) located in a low humidity room. The relative humidity of the room remained about 28% between about 21 and 27°C (70 and 80°F). The press was fitting with tooling to make about 5.7 cm (2.25 inch) diameter tablets. After pressure and size adjustments, tablets were made of about 21 grams with good tablet integrity. Hardnesses, as measured on a RIMAC tester, were to about 9.5 kg (21 lbs) force. Tablets were found to have picked up less than 0.3 wt.-% moisture during this operation.

14

The tablets had thicknesses of about 0.8 to 0.9 centimeters. The tablets dissolved under mild agitation in water in about 7 to 9 minutes and the resulting liquid did not deposit any residue when passed through 150 micron sieve (100 mesh).

5

Whereas particular embodiments of the invention have been described above for purposes of illustration, it will be appreciated by those skilled in the art that numerous variations of the details may be made without departing from the invention as described in
10 the appended claims.

Example 11

A mepiquat chloride powder prepared by the method of (example 8
15 for drum dryer) was tabletted (by a Carver press for example). Press pressure was varied at 6 to 7 metric tons, 8 to 9 metric tons, and 10 to 11 metric tons for durations of 1 minute each. The formed tablets, of 2.26 inches in diameter, had thicknesses between 6.1 and 6.6 mm (0.24 and 0.26 inches) with weights of
20 between 15.3 to 15.6 gms, with breaking strengths between 4 and 10 kgs (9 and 22.3 lbs) as determined on a modified Chatillon electronic tester, model DFI-50 mounted on a model LTC manual test stand. The tablets were dissolved in 750 ml of 342 ppm hardness water stirred with a magnetic stirring bar and dissolved
25 completely in 0.9 to 4.7 minutes.

Example 12

A mepiquat chloride powder prepared by the method of (example 9
30 for the Littleford dryer) was tabletted (in a Carver press for example). Press pressure was varied at 8 to 9 metric tons, and 10 to 11 metric tons for durations of 1 minute each. The formed tablets, of 2.26 inches in diameter, had thicknesses between 6.1 and 6.6 mm (0.24 and 0.26 inches) with weights of between 15.3
35 to 15.7 gms, with breaking strengths between 7.7 and 14.5 kgs (17 and 32 lbs) as determined on a modified Chatillon electronic tester, model DFI-50 mounted on a model LTC manual test stand. The tablets were dissolved in 750 ml of 342 ppm hardness water stirred with a magnetic stirring bar and dissolved completely in 4.4
40 to 5.8 minutes.

Example 13

A mepiquat chloride powder prepared by the method of (example 7
45 for the spray dryer) was tabletted (in a Carver press for example). Press pressure was varied at 6 to 7 metric tons, 8 to 9 metric tons, and 10 to 11 metric tons for durations of 1 minute

15

each. The formed tablets, of 5.74 cms (2.26 inches) in diameter, had thicknesses between 5.8 and 7.1 mms (0.23 and 0.28 inches) with weights of between 14.4 to 15.7 gms, with breaking strengths between 7.48 and 24.9 kgs (16.5 and 55 lbs) as determined on a
5 modified Chatillon electronic tester, model DFI-50 mounted on a model LTC manual test stand. The tablets were dissolved in 750 ml of 342 ppm hardness water stirred with a magnetic stirring bar and dissolved completely in 3.8 to 4.8 minutes.

10 Whereas particular embodiments of the invention have been described above for purposes of illustration, it will be appreciated by those skilled in the art that numerous variations of the details may be made without departing from the invention as described in the appended claims.

15

20

25

30

35

40

45

Claims

What is claimed is:

- 5 1. A plant growth regulator formulation in solid form comprising an effective amount of a hygroscopic plant growth regulator.
- 10 2. The formulation of claim 1 wherein said plant growth regulator is mepiquat chloride or chlormequat chloride.
- 15 3. A method of making a dry, flowable powder of an aqueous hygroscopic plant growth regulator using a spray dryer comprising: drying said hygroscopic plant growth regulator and mixing an effective amount of an inert.
- 20 4. A method of making, a dry, flowable powder of a hygroscopic plant growth regulator using a spray dryer comprising: injecting aqueous plant growth regulator feed solution into said spray dryer at a controlled rate; and injecting an inert in the inlet air stream of said spray dryer at a controlled rate; whereby the inert adheres to droplets of said plant growth regulator forming a dry, flowable powder.
- 25 5. A method of making a dry, flowable powder of a hygroscopic plant growth regulator using a double drum dryer comprising: charging aqueous plant growth regulator feed solution into said double drum dryer with interior pressurizing means and scraping means, at a continuous rate; rotating each drum of
30 said double drum dryer toward the other which deposits a portion of the aqueous plant growth regulator feed solution on the interior drum surface, and forms a solid film of plant growth regulator; removing said solid film by scraping means to form a dry, flowable powder.
- 35 6. A method of making a dry, flowable powder of a hygroscopic plant growth regulator using a batch vacuum dryer comprising: charging aqueous plant growth regulator feed solution into said batch vacuum dryer with chopping means, agitation means
40 and steam jacket, at a controlled rate; applying steam to said jacket; applying a vacuum to said batch vacuum dryer by a vacuum means; agitating said feed solution in said batch vacuum dryer; evaporating the water from said aqueous plant growth regulator feed solution thereby forming a paste; and
45 chopping said paste to form a dry, flowable powder.

17

7. A powder formed by one of the methods of claims 3 to 6.
8. A tablet formed from the powder of claim 7.
- 5 9. A water soluble bag comprising the powder of claim 7.

10

15

20

25

30

35

40

45

High Concentrated, Solid Mepiquat Chloride and Chlormequat
Chloride Products

5 Abstract of the Disclosure

The present invention provides hygroscopic plant growth regulator formulations in solid forms and associated methods of making the powders and tablets. The most preferred formulation uses an
10 effective amount of an N,N-dimethyl-piperidinium and/or N,N-dimethylammonium salt.

15

20

25

30

35

40

45

AMENDED CLAIMS

[received by the International Bureau on 09 December 1994 (09.12.94);
original claims 1,2,3-6 amended; remaining claims unchanged;
claims renumbered 1-8 (2 pages)]

1. A plant growth regulator formulation in solid form comprising a synthetic amorphous silicon dioxide hydrate and an effective amount of 1,1-dimethylpiperidinium chloride.
2. A method of making a plant growth regulator formulation as claimed in claim 1, using a spray drier comprising:
 - (i) drying 1,1-dimethylpiperidinium chloride and
 - (ii) mixing an effective amount of a silica.
3. A method of making a plant growth regulator formulation as claimed in claim 1, using a spray drier comprising:
 - (i) injecting an aqueous feed solution of 1,1-dimethylpiperidinium chloride into said spray drier at a controlled rate; and
 - (ii) injecting a silica into the inlet air stream of said spray drier at a controlled rate.
4. A method of making a plant growth regulator formulation as claimed in claim 1, using a double drum drier comprising:
 - (i) charging an aqueous feed solution of 1,1-dimethylpiperidinium chloride into said double drum drier with interior pressurizing means and scraping means, at a continuous rate;
 - (ii) rotating each drum of said double drum drier toward the other;
 - (iii) removing the solid film formed on the interior drum surface by scraping means.

5. A method of making a plant growth regulator formulation as claimed in claim 1, using a batch vacuum drier comprising:
 - (i) charging aqueous feed solution of 1,1-dimethylpiperidinium chloride into said batch vacuum drier with chopping means, agitation means and steam jacket, at a controlled rate;
 - (ii) applying steam to said jacket;
 - (iii) applying a vacuum to said batch vacuum drier by a vacuum means;
 - (iv) agitating said aqueous feed solution in said batch vacuum drier;
 - (v) evaporating the water from said aqueous feed solution; and
 - (vi) pulverizing the paste formed in step (v) by chopping.
6. A powder formed by one of the methods of claims 2 to 5.
7. A tablet formed from the powder of claim 6.
8. A water soluble bag comprising the powder of claim 6.

FIG. 1

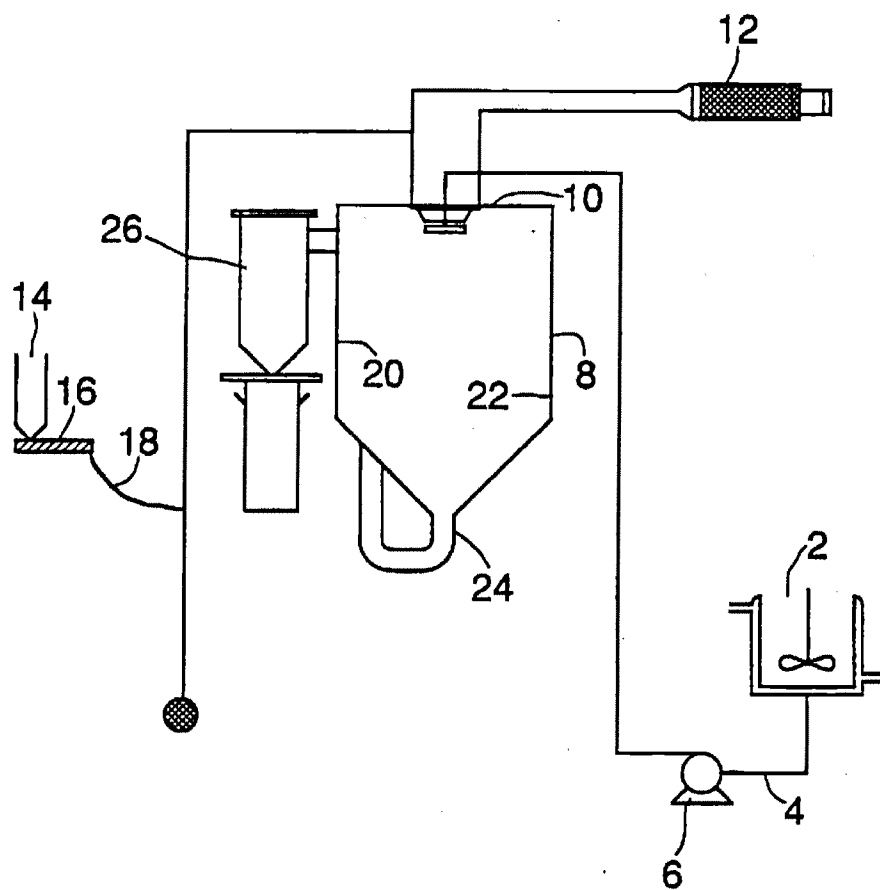


FIG.2

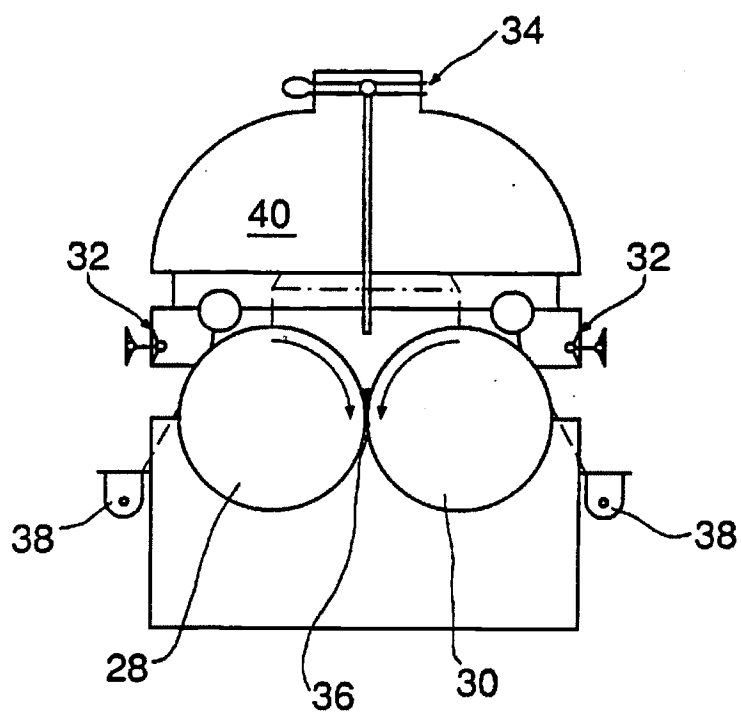
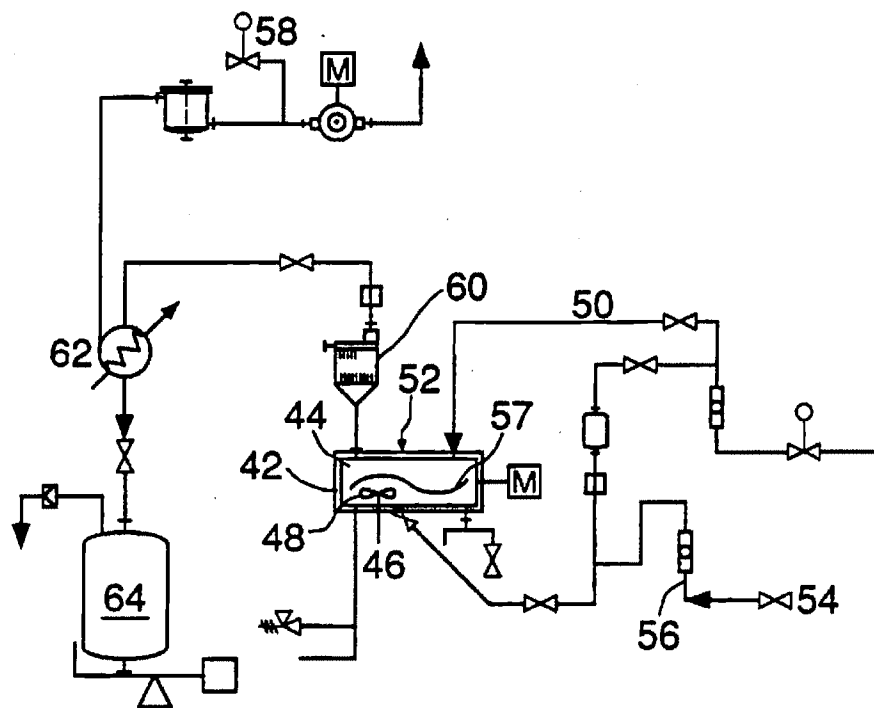


FIG.3



INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/EP 94/02253

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N43/40 A01N33/12 A01N25/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DD,A,101 386 (E. FIBITZ ET AL.) 5 November 1973 see page 2 - page 3 ---	1-9
X,P	EP,A,0 573 177 (MICRO-FLO) 8 December 1993 ---	1,2,7-9
X,P	WO,A,94 09627 (BASF) 11 May 1994 see page 1, line 19 - page 2, line 20 ---	1,2
X	FR,A,2 172 418 (BASF) 28 September 1973 see page 3, line 36 see page 5, line 34 - line 36 ---	1,2,7,8
A	US,A,3 356 569 (D.O. NICODEMUS ET AL.) 5 December 1967 see column 1, line 37 - column 2, line 23 ---	4
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 October 1994

Date of mailing of the international search report

07.11.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Decorte, D

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 94/02253

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP,A,0 518 629 (RHONE-POULENC AGROCHEMIE) 16 December 1992 see page 1, line 24 - line 27 see page 4, line 32 - line 33 -----</p>	9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 94/02253

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DD-A-101386		NONE	
EP-A-0573177	08-12-93	NONE	
WO-A-9409627	11-05-94	AU-B- 5150893	24-05-94
FR-A-2172418	28-09-73	DE-A- 2207575	23-08-73
		AT-B- 321026	10-03-75
		BE-A- 795534	16-08-73
		CH-A- 567353	15-10-75
		GB-A- 1414259	19-11-75
		JP-C- 1157912	25-07-83
		JP-A- 48088230	19-11-73
		JP-B- 57045203	27-09-82
		NL-A- 7301819	21-08-73
		SE-B- 382154	19-01-76
		US-A- 3905798	16-09-75
US-A-3356569		BE-A- 663212	29-10-65
		FR-A- 1508063	
		GB-A- 1095985	
		NL-A- 6505570	29-11-65
EP-A-0518629	16-12-92	US-A- 5139152	18-08-92
		AU-A- 1802392	24-12-92
		AU-A- 1809192	17-12-92
		AU-A- 1809292	17-12-92
		CA-A- 2071075	12-12-92
		CA-A- 2071076	12-12-92
		CA-A- 2071077	12-12-92
		CN-A- 1067859	13-01-93
		CN-A- 1067630	06-01-93
		CN-A- 1067629	06-01-93
		EP-A- 0524721	27-01-93
		EP-A- 0522713	13-01-93
		JP-A- 5155705	22-06-93
		JP-A- 5155704	22-06-93
		JP-A- 5155708	22-06-93
		NZ-A- 243095	27-09-94
		NZ-A- 243096	27-09-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. nat. Application No

PCT/EP 94/02253

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0518629		US-A- 5280835	25-01-94
		AU-A- 1755192	02-11-92
		AU-A- 1762292	02-11-92
		BR-A- 9205843	26-07-94
		BR-A- 9205844	26-07-94
		CN-A- 1066826	09-12-92
		CN-A- 1065575	28-10-92
		CZ-A- 9302050	16-03-94
		EP-A- 0579741	26-01-94
		EP-A- 0577755	12-01-94
		HU-A- 65187	02-05-94
		JP-T- 6507163	11-08-94
		JP-T- 6506898	04-08-94
		NZ-A- 242215	26-07-94
		NZ-A- 242216	27-06-94
		PT-A- 100335	29-04-94
		WO-A- 9217383	15-10-92
		WO-A- 9217385	15-10-92
		US-A- 5323906	28-06-94
		US-A- 5351831	04-10-94
		US-A- 5222595	29-06-93
		US-A- 5253759	19-10-93
		US-A- 5224601	06-07-93